

PATENT ABSTRACTS OF JAPAN

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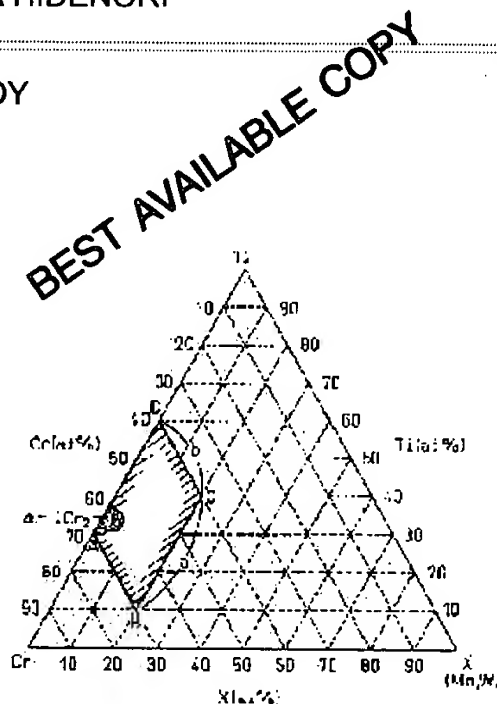
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(54) PRODUCTION OF BCC TYPE HYDROGEN STORAGE ALLOY

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a BCC type hydrogen storage alloy excellent in hydrogen occluding and releasing property while obviating the necessity of heat treatment and crushing stages by rapidly solidifying a molten Ti-Cr alloy of specific composition in an inert gas atmosphere by using a twin-roll method, a single-roll method, an atomizing method, etc.

SOLUTION: A molten alloy, having a composition enclosed with line segments obtained by connecting points A(Ti30Cr70), B (Ti10Cr70X20), C(Ti40Cr40 X20), and D(Ti60Cr40) in the ternary diagram and represented by the formula $Ti_{100-a-b}Cr_aX_b$ [where X is at least either of Mo and W and the symbols (a) and (b) satisfy, by atomic %, $40 \leq a \leq 70$ and $0 < b \leq 20$, respectively], is prepared. This molten alloy is rapidly solidified in an inert gas atmosphere by using a rotary body rotating at high speed or by means of an atomizing method and formed into a state of BCC phase at room temp. At this time, it is preferable to regulate cooling rate at the time of cooling to $\geq 102K/sec$. Owing to this composition, the BCC phase as nonequilibrium phase can be obtained at room temp. without requiring heat treatment stage.



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CLAIMS

[Claim(s)]

[Claim 1] It is the manufacture method of a BCC type hydrogen storing metal alloy that general formula $Ti_{100-a-b}Cr_aX_b$, however X are at least one sort of Mo and W, and composition is characterized by cooling quickly the alloy molten metal of the composition with which the inside a and b of a formula is atomic % display and it is expressed with $40 \leq a \leq 70$ and $0 < b \leq 20$ in inert gas atmosphere, and being it in the state of a BCC phase at a room temperature.

[Claim 2] The manufacture method of the BCC type hydrogen storing metal alloy characterized by for quick cooling being the congruence rolling method, the piece rolling method, or the atomizing method, and the cooling rate at the time of cooling being more than 102 K/sec in a claim 1.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] About the manufacture method of a hydrogen storing metal alloy, by quenching directly from a molten metal, even if especially this invention does not heat-treat, it maintains the state of a BCC phase at a room temperature, and it relates to the manufacture method of the BCC type hydrogen storing metal alloy which enables improvement of hydrogen *****.

[0002]

[Description of the Prior Art] As a storage / transportation means of hydrogen, a hydrogen storing metal alloy It is possible to carry out occlusion of the hydrogen gas of about 1000 times or more of own volume of an alloy, and to store it. as this hydrogen-absorption material LaNi₅ by which the metal of body centered cubic structures (Following BCC is called), such as V, Nb, Ta, and a TiVMn system, a TiVCr system alloy, is already put in practical use etc. -- AB₅ type alloy and TiMn₂ etc. -- AB₂ Compared with the type alloy, carrying out occlusion of a lot of hydrogen was known for many years. The hydrogen storing metal alloy which has the capacity of equivalent level, without including V to this since all contain expensive V, although the BCC type hydrogen storing metal alloy containing such Ti is high capacity can expect an epoch-making cost merit in the application which needs a high capacity hydrogen tank [for EV] hydrogen storing metal alloy.

[0003] In Japanese Patent Application No. No. 273438 [eight to] for which this invention person etc. applied previously, general formula Ti_{100-a-b}Cr_aX_b, however X were at least one sort of Mo and W, and the inside a and b of a formula is atomic % display, and proposed $40 \leq a \leq 70$ and the hydrogen storing metal alloy expressed with $0 < b \leq 20$. In order to freeze the BCC (body centered cubic structure) phase which is an elevated-temperature stable phase in ordinary temperature, manufacture of this BCC type hydrogen storing metal alloy usually has many which need to hold at 1200-1400 degrees C for 1 to 5 hours, and need to be cooled in an oil or iced water, after dissolving and casting a hardener.

[0004] Furthermore, in order to consider as the state in which hydrogen ***** is possible, it is necessary to grind an alloy to about dozens of microns, and needs to be activated in hydrogen atmosphere. The method of manufacturing the alloy-powder end of the negative-electrode material of a nickel hydrogen rechargeable battery by gas atomization is indicated by JP,6-192712,A as the direct manufacture method of raw material powder as a method of controlling a mean particle diameter and skipping trituration and a classification process, about this point. However, in manufacture of the hydrogen storing metal alloy as a common alloy, four processes of the dissolution and casting of a hardener, heat treatment, trituration, and activation are needed. However, at these four processes, development of the manufacture method the aforementioned heat treatment and whose ellipsis of 2 of a trituration process processes simplifying as much as possible from manufacture efficiency and the point of cost enables required therefore was desired.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention examines the quenching process for having a BCC phase and coming by the room temperature as a BCC type hydrogen storing metal alloy, and is to offer the manufacture method of the BCC type hydrogen storing metal alloy which makes an ellipsis possible for heat treatment and a trituration process simultaneously.

[0006] Moreover, other purposes of this invention examine roll quenching as the aforementioned quenching process, increase the touch area of a ribbon base and nothing hydrogen gas in an alloy, and are to offer the manufacture method of the BCC type hydrogen storing metal alloy which makes activation easy. Furthermore, another purpose of this invention is to offer the manufacture method of the BCC type hydrogen storing metal alloy which was excellent in hydrogen ***** whose application in a industrial scale is enabled with the alloy

which enables manufacture of the hydrogen storing metal alloy which has the hydrogen ***** of the high capacity as an alloy property at a low cost.

[0007]

[Means for Solving the Problem] As for the above-mentioned purpose, composition of general formula $Ti_{100-a-b}Cr_aX_b$, however X is at least one sort of Mo and W, and the inside a and b of a formula is atomic % display, and it is attained by the manufacture method of the BCC type hydrogen storing metal alloy characterized by cooling quickly $40 \leq a \leq 70$ and the alloy molten metal of the composition expressed with $0 < b \leq 20$ in inert gas atmosphere, and being them in the state of a BCC phase at a room temperature. Moreover, the aforementioned quick cooling is the congruence rolling method, the piece rolling method, or the atomizing method, and the above-mentioned purpose is attained also by the manufacture method of the BCC type hydrogen storing metal alloy characterized by the cooling rate at the time of cooling being more than 102 K/sec.

[0008]

[Embodiments of the Invention] As alloy composition of this invention, the range of a Ti-Cr-X system alloy is shown in drawing 2. this 3 yuan state diagram -- TiCr₂ of a Ti-Cr system it is -- the single phase field of C14 Laves phase existed, and this invention has avoided this range On the other hand, the alloy in which melting was carried out by the IH method, the arc solution process, etc. usually metamorphoses into more stable C14 Laves phase below 1200 degrees C at the time of cooling. in order [for this reason,] to form a BCC phase with the above-mentioned composition in this invention -- an elevated temperature -- a stable BCC phase -- up to ordinary temperature -- freezing -- an alloy -- homogeneity -- it considers as the range which consists of a BCC phase namely, within the limits surrounded by the segment which consists of the points A (Ti₃₀Cr₇₀) and B (Ti₁₀Cr₇₀X₂₀) of drawing 2, C (Ti₄₀Cr₄₀X₂₀), and D (Ti₆₀Cr₄₀) -- however, segments other than AD -- it considers as composition including a top

[0009] After the spinodal decomposition has decomposed into the detailed two phase of nano order regularly in the interior also in a BCC alloy in an old this invention person's etc. knowledge, a hydrogen-desorption property is influenced remarkably. the duality used as the foundations of this ternary alloy -- it is a system state diagram and it turns out especially by the Ti-Cr system, the Cr-Mo system, and the Cr-W system that the field of two-phase separation exists The state diagram of the duality of a Ti-Cr system is shown in drawing 3 as an example. It sets to this drawing and is TiCr₂. There is the solidus line of the two-phase separation which connects 1370 degrees C and the eutectic point, and it is a uniform BCC phase at the temperature beyond this. In this invention, it makes it possible to manufacture the ribbon-base alloy with which it quenched and had this state to the room temperature, and it is a BCC phase and the hydrogen-desorption property has been remarkably improved by this thing.

[0010] Furthermore, by considering as the thickness of 50-100 micrometers, and width of face of about 3-4mm, even if the aforementioned ribbon-base alloy enlarges specific surface area, and increases a direct touch area with the hydrogen gas at the time of hydrogenation and it does not grind it, it shall fully be activable. This quenching method is a kind of the melt quenching method suitable for industrial production, for example, the congruence rolling method, the piece rolling method, or the atomizing method is included, and the cooling rate in that case is carried out to more than 102 K/sec. In this melt quenching method, a predetermined alloy is dissolved with an electric furnace or a RF fusion furnace, the melting alloy is made to blow off from the nozzle at the nose of cam of a crucible by gas **, and contact solidification is carried out on the front face of the body of revolution for cooling which carries out high-speed rotation. The outline of the manufacturing installation of this invention is shown in drawing 1.

[0011] In order to prevent the oxidization which can be set even from the molten metal from atmosphere to a product, the roll 4 made from Cu is formed as an injection nozzle 2, a high frequency coil 3, and quenching equipment into it by making the whole equipment into the inert gas atmosphere 1. It dissolves according to the induced current which generates the hardener adjusted to alloy composition of this invention by the high frequency coil 3. It is carried out in the injection nozzle 2 made from refractories, for example like drawing 1, and it constitutes from this dissolution so that a dissolution alloy may be supplied continuously and may be injected in a fixed flow and pressure requirement. It is advantageous to stirring fully being made and making the component of a molten metal 8 uniform in the dissolution by the induced current by the high frequency coil 3. Especially in this invention, dissolution equipment is not limited and the dissolution and cooling should just be continuously made by the inert atmosphere.

[0012] For example, on the roll 4 made from Cu as body of revolution for cooling which carries out high-speed rotation like an arrow 5, the molten-metal style 8 is extended thinly and carries out the rapid solidification of the quenching equipment. The cooling rate in this case is decided for this thickness depending on the weighted solidity (a heat transfer rate, heat capacity, etc.) as the quality of the material of this body of revolution for cooling, and the

thickness of the molten-metal style 8 with the properties (the diameter of a nozzle, pressure, etc.) relevant to the amount of jet molten metals decided by the physical-properties value of the molten metal by alloy composition, and the peripheral speed of body of revolution. for example, the case where a molten metal Q is made to blow off on the roll 4 made from Cu which carries out high-speed rotation at speed V -- $Q \propto \pi a^2 p$ (the diameter of a nozzle, p: injection pressure) -- supposing it is expressed with a relation and thickness t and the quenching ribbon 6 of width of face w are obtained by this, it is expressed as relational expression of $Q \propto wtV$. In this invention, an alloy content is set constant, the relation of the calculated value from the aforementioned relational expression and actual manufacture is grasped, and the manufacture conditions which make the condition the optimal are acquired.

[0013] Next, the reason for component limitation of this invention is explained. For the inside a and b of Mo and/or W, and a formula, this alloy is atomic % display, and general formula $Ti_{100-a-b}Cr_x$, however X are expressed with $40 \leq a \leq 70$ and $0 < b \leq 20$. In the aforementioned composition range, it has the uniform phase of a BCC phase, distortion of the crystal structure in the two-phase separation state after quenching for coming with this to a room temperature and in an alloy is optimized, and it is adjusted to the detailed organization which enables promotion of the mobility of the hydrogen as a hydrogen storing metal alloy.

[0014] That is, the equilibrium pressure force [in / the hydrogen ***** (pressure composition constant-temperature-line-CT diagram) of a hydrogen storing metal alloy / less than / 40at% / in Cr] is low, and it becomes difficult to take out again the hydrogen which carried out occlusion in ordinary temperature. Moreover, in 70at% **, the aforementioned equilibrium pressure force has high Cr, and there is little hydrogen storage capacity in ordinary temperature. Furthermore, an alloy is not BCC-ized even if Mo and/or W heat-treat at 0at%. Since hydrogen storage capacity falls, it becomes moreover, less practical in 20at% **. For this reason, it limited to the above-mentioned composition range.

[0015] this invention prescribed the quenching conditions as the manufacture method so that hydrogen ***** might serve as the maximum in the state where it appeared uniformly, in the BCC phase of the aforementioned alloy. That is, in the cooling rate after the dissolution of a hardener, in the congruence rolling method, the piece rolling method, or the atomizing method, since it became difficult to freeze a BCC phase uniformly and desired hydrogen ***** was not obtained, the case of under 102 K/sec was limited to the cooling rate more than 102 K/sec. Moreover, it is because a problem does not actualize in quality of the material especially except that the effect of a uniform freeze of a BCC phase is saturated with this alloy system, though it is made remarkable super-quenching not to limit especially the upper limit of a cooling rate in this invention. However, increase of quenching processing cost will be caused with increase of a cooling rate, and it is not advantageous.

[0016] As mentioned above, although it is a BCC phase as a parent phase in this invention composition, it is easy to generate C14 Laves phase at a room temperature. However, before BCC of a parent phase appears as a solidification structure from a molten metal by cooling quickly and the transformation to C14 Laves phase is performed further after that, it results in a room temperature. Therefore, the BCC phase as a non-balancing phase is obtained at a room temperature, without passing through a heat treatment process. Below, this invention is further explained in full detail based on an example.

[0017]

[Example] At the example of this invention, it is $Ti_{39}Cr_{54}Mo_7$ of this invention range about composition of a hydrogen storing metal alloy. And the quality governing was carried out to $Ti_{41}Cr_{56}W_3$. In the example of this invention, the amount of dissolutions was carried out in 6g/time, it dissolved at 1800 degrees C, and the cooling roller checked that the cooling rate at this time was more than 102 K/sec by setting diameter: of roll 200mm, rotational frequency: 4000rpm, and the initial temperature of a roll as a room temperature. The quenching ribbon configurations acquired after cooling were thickness: 50-100micrometer, width-of-face: 3-4mm, and length: 30-40mm. The example of comparison is the arc dissolution and used what produced the 20g button ingot by diameter: 2cm, and was ground to 10mm angle grade after that.

[0018] Moreover, composition of each phase in an alloy was performed using EDX (energy-dispersion type X diffraction) of a transmission electron microscope and attachment. Moreover, measurement of the rate of a phase molar fraction created the crystal structure model based on the information acquired with the transmission electron microscope, and performed lied belt analysis of powder X diffraction data. Lied belt analysis can be asked for the weight fraction of each phase by calculation while it can carry out elaboration of the crystal structure parameter using diffraction intensity unlike the usual X-ray diffraction method. Analysis soft RIETAN94 which the National Institute for Research in Inorganic Materials spring doctor developed was used for lied belt analysis. The BCC phase / Laves-phase molar fraction of the quenching ribbon alloy of the example of this invention created by this invention and the arc dissolution alloy made into the example of comparison of this composition are shown in Table 1.

[0019]

[Table 1]

組 成	製造方法	B C C 相	ラーベス相	備 考
Ti ₃₉ Cr ₅₄ Mo ₇	ロール急冷	9 2	8	本発明例
	アーク溶解	2 0	8 0	比較例
Ti ₄₁ Cr ₅₆ W ₃	ロール急冷	8 9	1 1	本発明例
	アーク溶解	0	1 0 0	比較例

[0020] The Laves-phase molar fraction of the arc dissolution alloy of Table 1 to the example of comparison is Ti39Cr54Mo7. The BCC phase molar fraction of the roll quenching alloy of the example of this invention is Ti39Cr54Mo7 to being RABESU single phase in 80% and Ti41Cr56 W3 then. In 92% and Ti41Cr56 W3, it turns out that it has BCC-ized then notably at 89%. Ti39Cr54Mo7 of the aforementioned composition of this example in Table 2 And the measurement result of 40-degree C hydrogen ***** is shown about the sample of the example of this invention of Ti41Cr56 W3, and the example of comparison.

[0021]

[Table 2]

組 成	製造方法	水素吸蔵量(cc/g)	水素放出量(cc/g)	備 考
Ti ₃₉ Cr ₅₄ Mo ₇	ロール急冷	2 4 8	2 0 9	本発明例
	アーク溶解	9 8	1 0	比較例
Ti ₄₁ Cr ₅₆ W ₃	ロール急冷	2 2 2	1 8 1	本発明例
	アーク溶解	7 5	4 0	比較例

[0022] 40 degrees C [in this component] hydrogen ***** The hydrogen storage capacity of the roll quenching alloy of the example of this invention is Ti39Cr54Mo7. Then 248 cc/g, At Ti41Cr56 W3, 222 cc/g and the amount of hydrogen desorption are Ti39Cr54Mo7. As opposed to being 181 cc/g in 209 cc/g and Ti41Cr56 W3 then The hydrogen storage capacity of the arc dissolution alloy of the example of comparison is Ti39Cr54Mo7. Then 96 cc/g, At Ti41Cr56 W3, 75 cc/g and the amount of hydrogen desorption are Ti39Cr54Mo7. At 10 cc/g and Ti41Cr56 W3, it is 40 cc/g and it turns out in the example of this invention that hydrogen ***** is improved.

[0023]

[Effect of the Invention] As explained above, according to this invention, manufacture of an alloy with a property equivalent to the heat treatable alloy conventional only by roll cooling is possible. Furthermore, a ribbon-base alloy is activated, even if a direct touch area with the hydrogen gas at the time of hydrogenation is large and does not grind, since specific surface area is very large. For this reason, four processes of hardener dissolution casting and heat treatment which are needed by the conventional manufacturing process, trituration, and activation can be shortened at two processes of alloy dissolution / roll quenching and activation. Therefore, according to this invention, a high capacity BCC type hydrogen storing metal alloy can be extremely manufactured by the low cost, and utilization to various uses is enabled.

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TECHNICAL FIELD

[The technical field to which invention belongs] About the manufacture method of a hydrogen storing metal alloy, by quenching directly from a molten metal, even if especially this invention does not heat-treat, it maintains the state of a BCC phase at a room temperature, and it relates to the manufacture method of the BCC type hydrogen storing metal alloy which enables improvement of hydrogen *****.

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PRIOR ART

[Description of the Prior Art] As a storage / transportation means of hydrogen, it is a hydrogen storing metal alloy. LaNi₅ by which it is possible to carry out occlusion of the hydrogen gas of about 1000 times or more of own volume of an alloy, and to store it, and the metal of body centered cubic structures (Following BCC is called), such as V, Nb, Ta, and a TiVMn system, a TiVCr system alloy, is already put in practical use as this hydrogen-absorption material etc. -- AB₅ type alloy and TiMn₂ etc. -- AB₂ Compared with the type alloy, carrying out occlusion of a lot of hydrogen was known for many years. The hydrogen storing metal alloy which has the capacity of equivalent level, without including V to this since all contain expensive V, although the BCC type hydrogen storing metal alloy containing such Ti is high capacity can expect an epoch-making cost merit in the application which needs a high capacity hydrogen tank [for EV] hydrogen storing metal alloy.

[0003] In Japanese Patent Application No. No. 273438 [eight to] for which this invention person etc. applied previously, general formula Ti_{100-a-b}Cr_aX_b, however X were at least one sort of Mo and W, and the inside a and b of a formula is atomic % display, and proposed $40 \leq a \leq 70$ and the hydrogen storing metal alloy expressed with $0 < b \leq 20$. In order to freeze the BCC (body centered cubic structure) phase which is an elevated-temperature stable phase in ordinary temperature, manufacture of this BCC type hydrogen storing metal alloy usually has many which need to hold at 1200-1400 degrees C for 1 to 5 hours, and need to be cooled in an oil or iced water, after dissolving and casting a hardener.

[0004] Furthermore, in order to consider as the state in which hydrogen ***** is possible, it is necessary to grind an alloy to about dozens of microns, and needs to be activated in hydrogen atmosphere. The method of manufacturing the alloy-powder end of the negative-electrode material of a nickel hydrogen rechargeable battery by gas atomization is indicated by JP,6-192712,A as the direct manufacture method of raw material powder as a method of controlling a mean particle diameter and skipping pulverization and a classification process, about this point. However, in manufacture of the hydrogen storing metal alloy as a common alloy, four processes of the dissolution and casting of a hardener, heat treatment, pulverization, and activation are needed. However, at these four processes, development of the manufacture method the aforementioned heat treatment and whose abbreviation of 2 of a pulverization process processes simplifying as much as possible from manufacture efficiency and the point of cost enables required therefore was desired.

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to this invention, manufacture of an alloy with a property equivalent to the heat treatable alloy conventional only by roll cooling is possible. Furthermore, a ribbon-base alloy is activated, even if a direct touch area with the hydrogen gas at the time of hydrogenation is large and does not grind, since specific surface area is very large. For this reason, four processes of hardener dissolution casting and heat treatment which are needed by the conventional manufacturing process, pulverization, and activation can be shortened at two processes of alloy dissolution / roll quenching and activation. Therefore, according to this invention, a high capacity BCC type hydrogen storing metal alloy can be extremely manufactured by the low cost, and utilization to various uses is enabled.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The purpose of this invention examines the quenching process for having a BCC phase and coming by the room temperature as a BCC type hydrogen storing metal alloy, and is to offer the manufacture method of the BCC type hydrogen storing metal alloy which makes an abbreviation possible for heat treatment and a pulverization process simultaneously.

[0006] Moreover, other purposes of this invention examine roll quenching as the aforementioned quenching process, increase the touch area of a ribbon base and nothing hydrogen gas in an alloy, and are to offer the manufacture method of the BCC type hydrogen storing metal alloy which makes activation easy. Furthermore, another purpose of this invention is to offer the manufacture method of the BCC type hydrogen storing metal alloy which was excellent in hydrogen ***** whose application in a industrial scale is enabled with the alloy which enables manufacture of the hydrogen storing metal alloy which has the hydrogen ***** of the high capacity as an alloy property at a low cost.

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MEANS

[Means for Solving the Problem] As for the above-mentioned purpose, composition of general formula $Ti_{100-a-b}Cr_aX_b$, however X is at least one sort of Mo and W, and the inside a and b of a formula is atomic % display, and it is attained by the manufacture method of the BCC type hydrogen storing metal alloy characterized by cooling quickly $40 \leq a \leq 70$ and the alloy molten metal of the composition expressed with $0 < b \leq 20$ in inert gas atmosphere, and being them in the state of a BCC phase at a room temperature. Moreover, the aforementioned quick cooling is the congruence rolling method, the piece rolling method, or the atomizing method, and the above-mentioned purpose is attained also by the manufacture method of the BCC type hydrogen storing metal alloy characterized by the cooling rate at the time of cooling being more than 102 K/sec.

[0008]

[Embodiments of the Invention] As alloy composition of this invention, the range of a Ti-Cr-X system alloy is shown in drawing 2. this 3 yuan state diagram -- $TiCr_2$ of a Ti-Cr system it is -- the single phase field of C14 Laves phase existed, and this invention has avoided this range On the other hand, the alloy in which melting was carried out by the IH method, the arc solution process, etc. usually metamorphoses into more stable C14 Laves phase below 1200 degrees C at the time of cooling. in order [for this reason,] to form a BCC phase with the above-mentioned composition in this invention -- an elevated temperature -- a stable BCC phase -- up to ordinary temperature -- freezing -- an alloy -- homogeneity -- it considers as the range which consists of a BCC phase namely, within the limits surrounded by the segment which consists of the points A ($Ti_{30}Cr_{70}$) and B ($Ti_{10}Cr_{70}X_{20}$) of drawing 2, C ($Ti_{40}Cr_{40}X_{20}$), and D ($Ti_{60}Cr_{40}$) -- however, segments other than AD -- it considers as composition including a top

[0009] After the spinodal decomposition has decomposed into the detailed two phase of nano order regularly in the interior also in a BCC alloy in an old this invention person's etc. knowledge, a hydrogen-desorption property is influenced remarkably. the duality used as the foundations of this ternary alloy -- it is a system state diagram and it turns out especially by the Ti-Cr system, the Cr-Mo system, and the Cr-W system that the field of two-phase separation exists The state diagram of the duality of a Ti-Cr system is shown in drawing 3 as an example. It sets to this drawing and is $TiCr_2$. There is the solidus line of the two-phase separation which connects 1370 degrees C and the eutectic point, and it is a uniform BCC phase at the temperature beyond this. In this invention, it makes it possible to manufacture the ribbon-base alloy with which it quenched and had this state to the room temperature, and it is a BCC phase and the hydrogen-desorption property has been remarkably improved by this thing.

[0010] Furthermore, by considering as the thickness of 50-100 micrometers, and width of face of about 3-4mm, even if the aforementioned ribbon-base alloy enlarges specific surface area, and increases a direct touch area with the hydrogen gas at the time of hydrogenation and it does not grind it, it shall fully be activable. This quenching method is a kind of the melt quenching method suitable for industrial production, for example, the congruence rolling method, the piece rolling method, or the atomizing method is included, and the cooling rate in that case is carried out to more than 102 K/sec. In this melt quenching method, a predetermined alloy is dissolved with an electric furnace or a RF fusion furnace, the melting alloy is made to blow off from the nozzle at the nose of cam of a crucible by gas **, and contact solidification is carried out on the front face of the body of revolution for cooling which carries out high-speed rotation. The outline of the manufacturing installation of this invention is shown in drawing 1.

[0011] In order to prevent the oxidization which can be set even from the molten metal from atmosphere to a product, the roll 4 made from Cu is formed as an injection nozzle 2, a high frequency coil 3, and quenching equipment into it by making the whole equipment into the inert gas atmosphere 1. It dissolves according to the induced current which generates the hardener adjusted to alloy composition of this invention by the high frequency coil 3. It is carried out in the injection nozzle 2 made from refractories, for example like drawing 1, and it

constitutes from this dissolution so that a dissolution alloy may be supplied continuously and may be injected in a fixed flow and pressure requirement. It is advantageous to stirring fully being made and making the component of a molten metal 8 uniform in the dissolution by the induced current by the high frequency coil 3. Especially in this invention, dissolution equipment is not limited and the dissolution and cooling should just be continuously made by the inert atmosphere.

[0012] For example, on the roll 4 made from Cu as body of revolution for cooling which carries out high-speed rotation like an arrow 5, the molten-metal style 8 is extended thinly and carries out the rapid solidification of the quenching equipment. The cooling rate in this case is decided for this thickness depending on the weighted solidity (a heat transfer rate, heat capacity, etc.) as the quality of the material of this body of revolution for cooling, and the thickness of the molten-metal style 8 with the properties (the diameter of a nozzle, pressure, etc.) relevant to the amount of jet molten metals decided by the physical-properties value of the molten metal by alloy composition, and the peripheral speed of body of revolution. for example, the case where a molten metal Q is made to blow off on the roll 4 made from Cu which carries out high-speed rotation at speed $V \sim Q \cdot \pi \cdot a^2 \cdot p$ (the diameter of a nozzle, p: injection pressure) -- supposing it is expressed with a relation and thickness t and the quenching ribbon 6 of width of face w are obtained by this, it is expressed as relational expression of $Q \cdot w \cdot t \cdot V$. In this invention, an alloy content is set constant, the relation of the calculated value from the aforementioned relational expression and actual manufacture is grasped, and the manufacture conditions which make the condition the optimal are acquired.

[0013] Next, the reason for component limitation of this invention is explained. For the inside a and b of Mo and/or W, and a formula, this alloy is atomic % display, and general formula $Ti_{100-a-b}Cr_x$, however x are expressed with $40 \leq a \leq 70$ and $0 < b \leq 20$. In the aforementioned composition range, it has the uniform phase of a BCC phase, distortion of the crystal structure in the two-phase separation state after quenching for coming with this to a room temperature and in an alloy is optimized, and it is adjusted to the detailed organization which enables promotion of the mobility of the hydrogen as a hydrogen storing metal alloy.

[0014] That is, the equilibrium pressure force [in / the hydrogen ***** (pressure composition constant-temperature-line-CT diagram) of a hydrogen storing metal alloy / less than / 40at% / in Cr] is low, and it becomes difficult to take out again the hydrogen which carried out occlusion in ordinary temperature. Moreover, in 70at% **, the aforementioned equilibrium pressure force has high Cr, and there is little hydrogen storage capacity in ordinary temperature. Furthermore, an alloy is not BCC-ized even if Mo and/or W heat-treat at 0at%. Since hydrogen storage capacity falls, it becomes moreover, less practical in 20at% **. For this reason, it limited to the above-mentioned composition range.

[0015] this invention prescribed the quenching conditions as the manufacture method so that hydrogen ***** might serve as the maximum in the state where it appeared uniformly, in the BCC phase of the aforementioned alloy. That is, in the cooling rate after the dissolution of a hardener, in the congruence rolling method, the piece rolling method, or the atomizing method, since it became difficult to freeze a BCC phase uniformly and desired hydrogen ***** was not obtained, the case of under 102 K/sec was limited to the cooling rate more than 102 K/sec. Moreover, it is because a problem does not actualize in quality of the material especially except that the effect of a uniform freeze of a BCC phase is saturated with this alloy system, though it is made remarkable super-quenching not to limit especially the upper limit of a cooling rate in this invention. However, increase of quenching processing cost will be caused with increase of a cooling rate, and it is not advantageous.

[0016] As mentioned above, although it is a BCC phase as a parent phase in this invention composition, it is easy to generate C14 Laves phase at a room temperature. However, before BCC of a parent phase appears as a solidification structure from a molten metal by cooling quickly and the transformation to C14 Laves phase is performed further after that, it results in a room temperature. Therefore, the BCC phase as a non-balancing phase is obtained at a room temperature, without passing through a heat treatment process. Below, this invention is further explained in full detail based on an example.

[Translation done.]

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EXAMPLE

[Example] At the example of this invention, it is Ti39Cr54Mo7 of this invention range about composition of a hydrogen storing metal alloy. And the quality governing was carried out to Ti41Cr56 W3. In the example of this invention, the amount of dissolutions was carried out in 6g/time, it dissolved at 1800 degrees C, and the cooling roller checked that the cooling rate at this time was more than 102 K/sec by setting diameter: of roll 200mm, rotational frequency: 4000rpm, and the initial temperature of a roll as a room temperature. The quenching ribbon configurations acquired after cooling were thickness: 50-100micrometer, width-of-face: 3-4mm, and length: 30-40mm. The example of comparison is the arc dissolution and used what produced the 20g button ingot by diameter: 2cm, and was ground to 10mm angle grade after that.

[0018] Moreover, composition of each phase in an alloy was performed using EDX (energy-dispersion type X diffraction) of a transmission electron microscope and attachment. Moreover, measurement of the rate of a phase molar fraction created the crystal structure model based on the information acquired with the transmission electron microscope, and performed lied belt analysis of powder X diffraction data. Lied belt analysis can be asked for the weight fraction of each phase by calculation while it can carry out [precise]-izing of the crystal structure parameter using diffraction intensity unlike the usual X-ray diffraction method. Analysis soft RIETAN94 which the National Institute for Research in Inorganic Materials spring doctor developed was used for lied belt analysis. The BCC phase / Laves-phase molar fraction of the quenching ribbon alloy of the example of this invention created by this invention and the arc dissolution alloy made into the example of comparison of this composition are shown in Table 1.

[0019]

[Table 1]

組 成	製造方法	B C C 相	ラーベス相	備 考
Ti ₃₉ Cr ₅₄ Mo ₇	ロール急冷	9 2	8	本発明例
	アーク溶解	2 0	8 0	比較例
Ti ₄₁ Cr ₅₆ W ₃	ロール急冷	8 9	1 1	本発明例
	アーク溶解	0	1 0 0	比較例

[0020] The Laves-phase molar fraction of the arc dissolution alloy of Table 1 to the example of comparison is Ti39Cr54Mo7. The BCC phase molar fraction of the roll quenching alloy of the example of this invention is Ti39Cr54Mo7 to being RABESU single phase in 80% and Ti41Cr56 W3 then. In 92% and Ti41Cr56 W3, it turns out that it has BCC-ized then notably at 89%. Ti39Cr54Mo7 of the aforementioned composition of this example in Table 2 And the measurement result of 40-degree C hydrogen ***** is shown about the sample of the example of this invention of Ti41Cr56 W3, and the example of comparison.

[0021]

[Table 2]

組 成	製造方法	水素吸蔵量(cc/g)	水素放出量(cc/g)	備 考
Ti ₃₉ Cr ₅₄ Mo ₇	ロール急冷	2 4 8	2 0 9	本発明例
	アーク溶解	9 6	1 0	比較例
Ti ₄₁ Cr ₅₆ W ₃	ロール急冷	2 2 2	1 8 1	本発明例
	アーク溶解	7 5	4 0	比較例

[0022] 40 degrees C [in this component] hydrogen ***** The hydrogen storage capacity of the roll quenching alloy of the example of this invention is Ti39Cr54Mo7. Then 248 cc/g, At Ti41Cr56 W3, 222 cc/g and the amount of hydrogen desorption are Ti39Cr54Mo7. As opposed to being 181 cc/g in 209 cc/g and Ti41Cr56 W3 then The hydrogen storage capacity of the arc dissolution alloy of the example of comparison is Ti39Cr54Mo7. At 96 cc/g and Ti41Cr56 W3, 75 cc/g and the amount of hydrogen desorption are Ti39Cr54Mo7 then. In 10 cc/g and Ti41Cr56 W3, it is 40 cc/g. In the example of this invention, it turns out that hydrogen ***** is improved.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the outline of the roll quenching equipment concerning this invention.

[Drawing 2] It is drawing showing composition by the 3 yuan state diagram of the TiCrX (Mo and/or W) system concerning this invention.

[Drawing 3] It is a Ti-Cr system binary-condition view relevant to this invention.

[Description of Notations]

- 1 -- Inert gas atmosphere
- 2 -- Injection nozzle
- 3 -- High frequency coil
- 4 -- Roll made from Cu
- 5 -- High-speed rotation
- 6 -- Quenching ribbon
- 7 -- Molten metal
- 8 -- Molten-metal style

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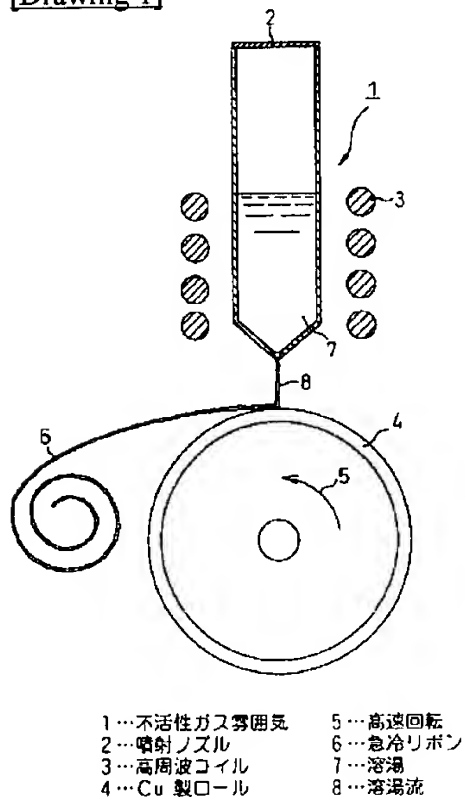
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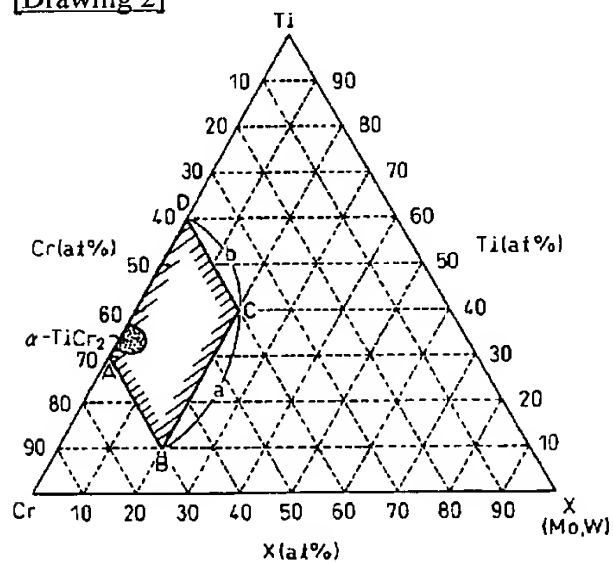
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DRAWINGS

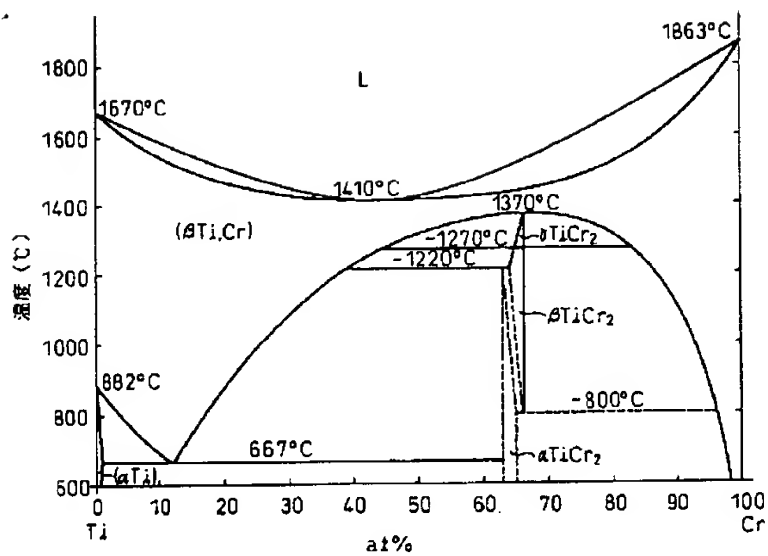
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]